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(54) IMPROVEMENTS RELATING TO THE CATALYTIC OXIDATION OF CARBON MONOXIDE

(71) We, BRITISH-AMERICAN TOBACCO COMPANY LIMITED, a Company incorporated under the laws of Great Britain, of Westminster House, 7, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention concerns improvements relating to the removal of carbon monoxide from gases, for example from tobacco smoke, by oxidation in the presence of a catalyst.

A large number of metallic oxides act as 15 oxidation catalysts and for most of them this property can be explained by the fact that they are readily reduced to the metals or to lower oxides by substances to be oxidized, and are readily oxidized directly 20 by oxygen. It is known that carbon monoxide can be oxidized by oxides of cobalt, copper, iron, lead and manganese at temperatures of from 300-1500°C. It is also known that catalytic oxidation of carbon 25 monoxide at low temperature can be brought about by certain metals, such as platinum and palladium, but the time of contact necessary for complete oxidation is long. Mixtures of metallic oxides have been found 30 to be effective and can bring about catalytic oxidation of carbon monoxide within a short time of contact at room temperature. For example, hopcalite, which is a mixture of manganese oxide and copper oxide catalyzes the reaction $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ at room 35 temperature.

It is well established that the method of preparation may be a critical factor for obtaining a product having required catalytic 40 properties. The literature shows that this is particularly applicable to the preparation of catalysts containing manganese oxide for the low-temperature oxidation of carbon monoxide. Failure to achieve reproducibly efficient catalysts may be attributable to a fun-

damental lack of knowledge of the mechanisms of the processes involved, both in the preparation and in the use of the catalysts. It is clear that the mechanisms can be related directly to the surface properties of 50 the catalyst. It is not, however, possible in general to predict the surface properties of the catalyst material from a knowledge of those of the bulk material. Two materials may therefore be prepared which, for ordinary 55 chemical purposes, are considered to be virtually identical, but which, due to subtle differences in surface character, exhibit profound differences in the speed and nature of chemical processes which occur at 60 their surfaces. An important corollary of this is that, because of the subtlety of difference in surface structure, which itself constitutes a very small part of the catalyst, 65 the catalytic properties observed are difficult to define in precise chemical terminology. Commonly, it may then be best to define the catalyst in terms of its preparation. This, however, has to be done as precisely 70 as possible in order to achieve reproducibility in the method of preparation.

According to the invention, in the production of a manganese-dioxide catalyst for the oxidation of carbon monoxide to carbon 75 dioxide for the purpose of removing the said monoxide from tobacco smoke or other gases or gas mixtures, manganese dioxide is prepared by precipitation from manganese sulphate tetrahydrate, nitric acid and potassium permanganate, the resultant precipitate is filtered, washed and dried and is 80 granulated or powdered, with or without prior compression, and the manganese dioxide thus prepared is freed from water by subjecting it to outgassing under vacuum. 85 Preferably, in addition, residual adsorbed water and oxygen may be removed from the surface of the manganese dioxide by the introduction and removal of carbon monoxide. 90

Particularly in the case of tobacco-smoke filters, a high vacuum may be employed.

An example for the production of an effective such manganese-dioxide catalyst will now be described. If the method described is followed, an extremely efficient catalyst can be reproducibly obtained.

Manganese sulphate tetrahydrate (44.6 g) is dissolved in water (500 ml) and concentrated nitric acid (50 ml) is added to the solution slowly with stirring. Powdered potassium permanganate (31 g) is added slowly with constant stirring and the mixture is allowed to stand for about 20 minutes. The precipitate is filtered on a Büchner funnel and the filter cake is washed with the minimum amount of distilled water to obtain a colourless filtrate. The precipitate, which is dried under ambient conditions, is then treated in one of two ways:

(i) the semi-dry cake is compressed at 30,000 pounds per square inch prior to granulation and sieving, or

(ii) granulation and sieving are carried out directly with the semi-dry precipitate without compression.

The material is granulated to a mesh-size range of 0.30-0.71 mm (22-52 mesh British Standard). In order to remove all traces of water, the granular product is outgassed in a vacuum chamber or system to an equilibrium pressure of 10^{-4} Torr and at a temperature below the sintering temperature, preferably at room temperature.

To prevent "poisoning" of the catalyst by water vapour either prior to use or during use and to increase its catalytic activity further, manganese dioxide prepared by the above method is given the following additional treatment. After the precipitate has been outgassed in vacuum, carbon monoxide is introduced in the chamber or system, whereby residual adsorbed water and oxygen is effectively removed from the surface of the catalyst. The chamber or system is then once more evacuated to a pressure of approximately 10^{-4} Torr and nitrogen gas is introduced at a pressure of 760 Torr in order to flush out residual carbon monoxide.

The nitrogen is removed by evacuating to a pressure of about 10^{-3} Torr and oxygen is introduced at a pressure of 760 Torr. The catalyst thus treated is retained in the oxygen atmosphere for a period ranging from 2 hours to 2 days. Without the above described additional treatment, the catalytic activity of the catalyst towards carbon monoxide was found to diminish rapidly on storage at ambient atmospheric conditions.

In order to investigate the efficiency, for the catalytic oxidation of carbon monoxide in tobacco smoke, of the granular catalyst prepared by the above-described method, 65 cigarettes were made up with filters each

comprising two sections of conventional filtering material and containing quantities of from 100 mg to 1000 mg of the catalyst. On smoking the cigarettes, percentages of from 30 to 90% respectively of carbon monoxide were found to have been removed from the smoke.

A further improvement in the removal of carbon monoxide from tobacco smoke was obtained by using a filter in which the manganese-dioxide catalyst contained, by weight, 8% of silver and 7% of copper added as nitrates to the manganese sulphate solution prior to the addition of the potassium permanganate to the said solution. On smoking a cigarette through a filter containing 500 mg of the resultant material about 70% of the carbon monoxide was removed.

Specific examples of the use of the afore-said granular catalyst for the filtration of cigarette smoke will now be described:

Example 1

Triple filters 30 mm long were prepared of which the two outer sections, each 5 mm long, were composed of conventional filtering material and the centre section, 20 mm long, of 500 mg of the granular manganese dioxide. The filters were attached to cigarettes which were smoked, using a smoking engine which provided one puff per minute of two seconds duration and of 35 ml volume. On analysis of the smoke from the cigarettes, it was found that 35% of the carbon monoxide had been removed.

Example 2

Similar filters were produced in which, however, the granular manganese-dioxide catalyst contained 8% Ag and 7% Cu by weight added in the form of silver nitrate and copper nitrate to the manganese sulphate solution prior to the addition of the potassium permanganate to the said solution. On smoking cigarettes through these filters, the reduction in carbon monoxide was found to be 60%.

Example 3

Triple filters 20 mm long of which the two outer sections, each 5 mm long, were composed of conventional filtering material and the centre section, 10 mm long, of 250 mg of the manganese dioxide gave a reduction in carbon monoxide of 10%.

Example 4

On smoking cigarettes through a filter similar to that of Example 3, but with contents, by weight, of 7% Ag and 8% Cu in the manganese dioxide catalyst, the reduction in carbon monoxide was 20%.

For the sake of comparison, triple filters were prepared consisting of two outer sec-

tions of conventional filtering material and a centre section of granular manganese dioxide which had not been prepared as described above and had been exposed to air for a few hours. The filters were attached to cigarettes which were smoked. On analysis of the smoke, it was found that the reduction in carbon monoxide was less than 10% irrespective of the amount of manganese dioxide used.

WHAT WE CLAIM IS:—

1. A method for the production of a manganese-dioxide catalyst for the oxidation of carbon monoxide to carbon dioxide for the purpose of removing the said monoxide from tobacco smoke or other gases or gas mixtures, wherein manganese dioxide is prepared by precipitation from manganese sulphate tetrahydrate, nitric acid and potassium permanganate, the resultant precipitate is filtered, washed and dried and is granulated or powdered, with or without prior compression, and the manganese dioxide thus prepared is freed from water by subjecting it to outgassing under vacuum.

2. A method as claimed in claim 1, wherein residual adsorbed water and oxygen are removed from the surface of the manganese dioxide by the introduction of carbon monoxide into the said dioxide and its removal therefrom together with said water and oxygen.

3. A method as claimed in claim 1 or 2, wherein the manganese dioxide is granulated to a mesh-size range 0.30-0.71 mm.

4. A method as claimed in any one of claims 1 to 3, wherein the outgassing under vacuum is performed at a pressure of 10^{-4} Torr and at a temperature below the sintering temperature.

5. A method as claimed in any one of claims 2 to 4, wherein the introduction and removal of carbon monoxide is followed by the introduction of and removal of nitrogen to flush out residual carbon monoxide.

6. A method as claimed in claim 5, wherein the manganese dioxide is finally retained for a period in an oxygen atmosphere.

7. A method as claimed in any one of claims 1 to 6, wherein silver and copper are included in the manganese-dioxide catalyst.

8. A method for the preparation of a catalyst as claimed in claim 1 for the oxidation of carbon monoxide to carbon dioxide for the purpose of removing the said monoxide from tobacco smoke substantially as hereinbefore described.

9. A catalyst for the oxidation of carbon monoxide to carbon dioxide when produced by a method as claimed in any one of claims 1 to 10.

10. A tobacco-smoke filter comprising a catalyst prepared by a method as claimed in any one of claims 1 to 10.

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